IFM-GEOMAR

Leibniz-Institut für Meereswissenschaften
an der Universität Kiel

IFM-GEOMAR Report 2002-2004

From the Seafloor to the Atmosphere

- Marine Sciences at IFM-GEOMAR Kiel -

June 2005

Preface

For the first time, the Leibniz Institute of Marine Sciences (IFM-GEOMAR) presents a joint report of its research activities and developments in the years 2002-2004. In January 2004 the institute was founded through a merger of the former Institute for Marine Research (IfM) and the GEOMAR Research Center for Marine Geosciences. This report addresses friends and partners in science, politics and private enterprises. It gives an insight into the scientific achievements of IFM-GEOMAR and its predecessor institutes during the last three years.

3.7 Marine Gas Hydrates

Gas hydrates are ice-like compounds in which small gas molecules are trapped inside a cage of water molecules (Fig. 1). Their formation requires low temperatures, high pressures, and enough gas to exceed saturation (Fig. 2). The trapped gas in natural gas hydrates is mostly methane, which is generated by the decay of organic matter. Gas hydrates are found in sediments with high gas productivity along continental margins and marginal seas in depths exceeding 300 - 500 and are nowadays a major focus of geo-marine research for the following reasons:

- More than 160 m^3 of gas can be stored in 1 m^3 of hydrate, i.e. the gas density is comparable to a filled compressed gas cylinder;
- The amount of energy stored in gas hydrates along the continental margins is suggested to be larger than, or at least similar to, the amount of energy stored in other known exploitable fossil energy reservoirs (i.e. coal, oil, and gas).
- The decomposition of hydrates (due to warming of bottom waters or decreasing sea level) has been suggested as a trigger or positive feedback for rapid global warming episodes in the Earth's history.
- Continental slope instability caused by hydrate decomposition is suggested as a trigger mechanism for underwater landslides and tsunami generation.

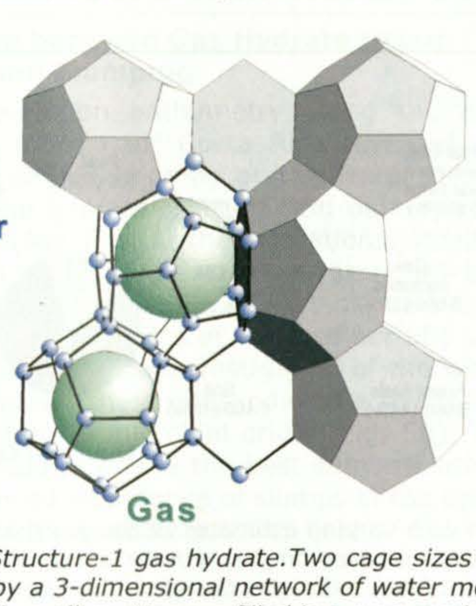

Fig. 1: Structure-1 gas hydrate.Two cage sizes are formed by a 3-dimensional network of water molecules. When all cavities are filled in a pure methane hydrate, the sum formula is approx. CH_4 5.7 H_2O.

Since the recovery of natural hydrates offshore Oregon by GEOMAR expedition *SONNE* 143 in 1996, Kiel has become one of the world's centres for research on natural gas hydrates. Two large-scale integrated projects within the Geotechnology program of BMBF have been coordinated within FB2 from 2001-2003 (LOTUS and OMEGA), with scientific expeditions to the Black Sea, the Gulf of Mexico, and the Hydrate Ridge, offshore Oregon. Former GEOMAR scientist Gerhard Bohrmann was co-chief of leg 204 of the Ocean Drilling Program, and found himself in the unusual role as a main character of the science fiction novel "Der Schwarm" by Frank Schätzing.

The following highlights, summarized here briefly, are representative of the scope of scientific knowledge gained from these projects.

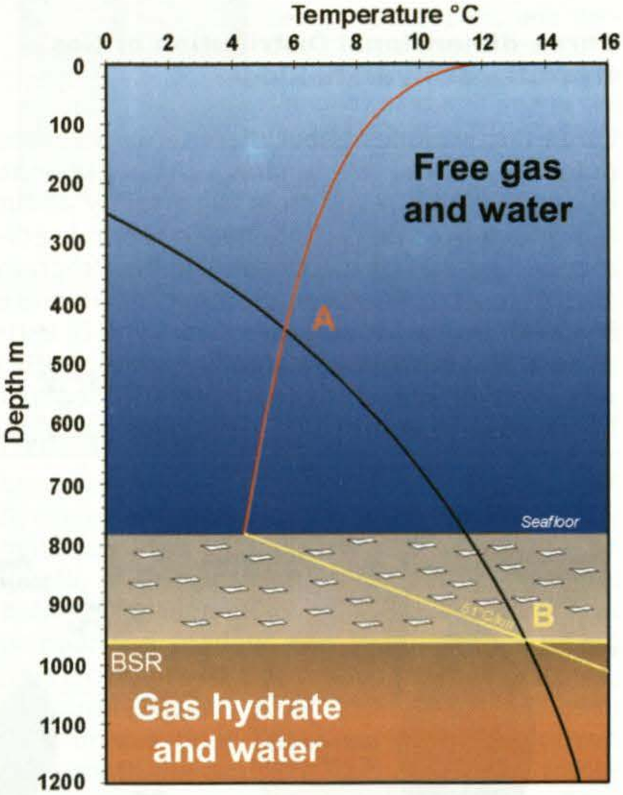

Figure 2: Stability of CH_4 hydrate in seawater. The black line is the phase boundary. Above this line, methane exceeding saturation in seawater is stable as a free gas phase; below, it will form hydrates. The red line indicates the temperature profile of seawater, the yellow line the geothermal gradient within the sediment. Hydrate is stable in the depth interval between points A and B.

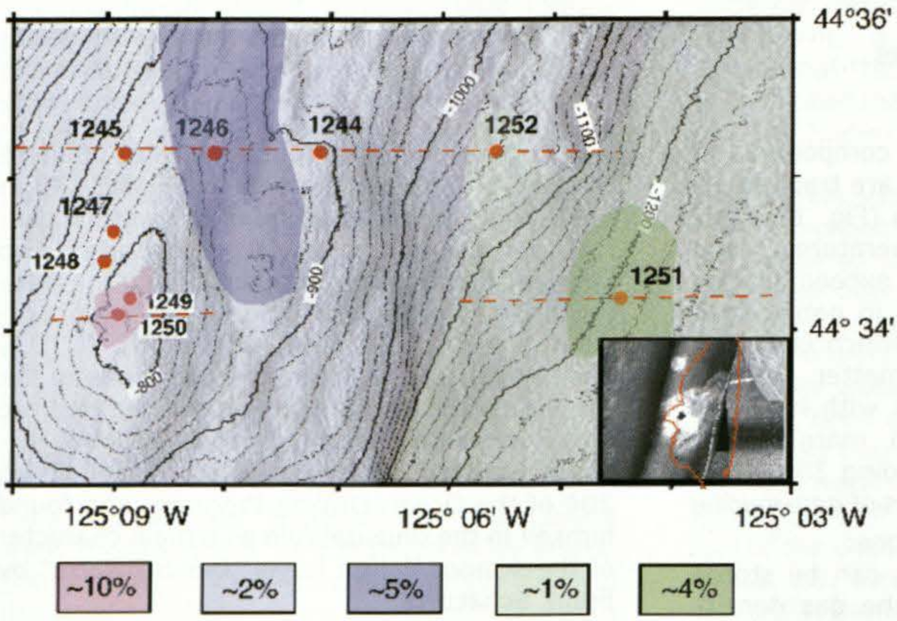

Figure 3: Fraction of the sediment occupied by gas hydrates averaged over the thickness of the gas hydrate stability field at the Southern Summit of Hydrate Ridge, Oregon. The numbers refer to the sites drilled during ODP Leg 204.

Three-dimensional Distribution of Gas Hydrates at Hydrate Ridge

Large uncertainties about the energy resource potential and the role in global climate change of gas hydrates result from uncertainty about how much hydrate is contained in marine sediments. Leg 204 of the Ocean Drilling Program (ODP) to the Southern Summit of Hydrate Ridge attempted to improve such type of estimates. The gas hydrate stability zone (GHSZ) was continuously sampled from the seafloor to its base in contrasting geological settings, which were defined by a 3D seismic survey. By integrating results from different methods, including several new techniques developed for Leg 204, it was possible to obtain a high-resolution, quantitative estimate of the total amount and spatial variability of gas hydrate in this structural system (Fig. 3).

The results unequivocally showed that high gas hydrate content (30–40% of pore space or 20–26% of total volume) is restricted to the upper tens of meters below the seafloor near the summit of the structure, where vigorous fluid venting occurs. Below that zone, the average gas hydrate content of the sediments in the GHSZ is generally <2% of the pore space. The small fraction of pore space filled by gas hydrates challenges the estimates of the global world-wide gas hydrate reservoir in the order of 1 x 10^5 GtC. A new global estimate resulting from this campaign, about an order of magnitude smaller (Fig. 4), questions the role of gas hydrates in driving global change or as an important future fossil fuel resource. High concentrations of gas hydrate, however, are present locally and may be of economic importance in the future and hence their accurate delineation needs to be pursued.

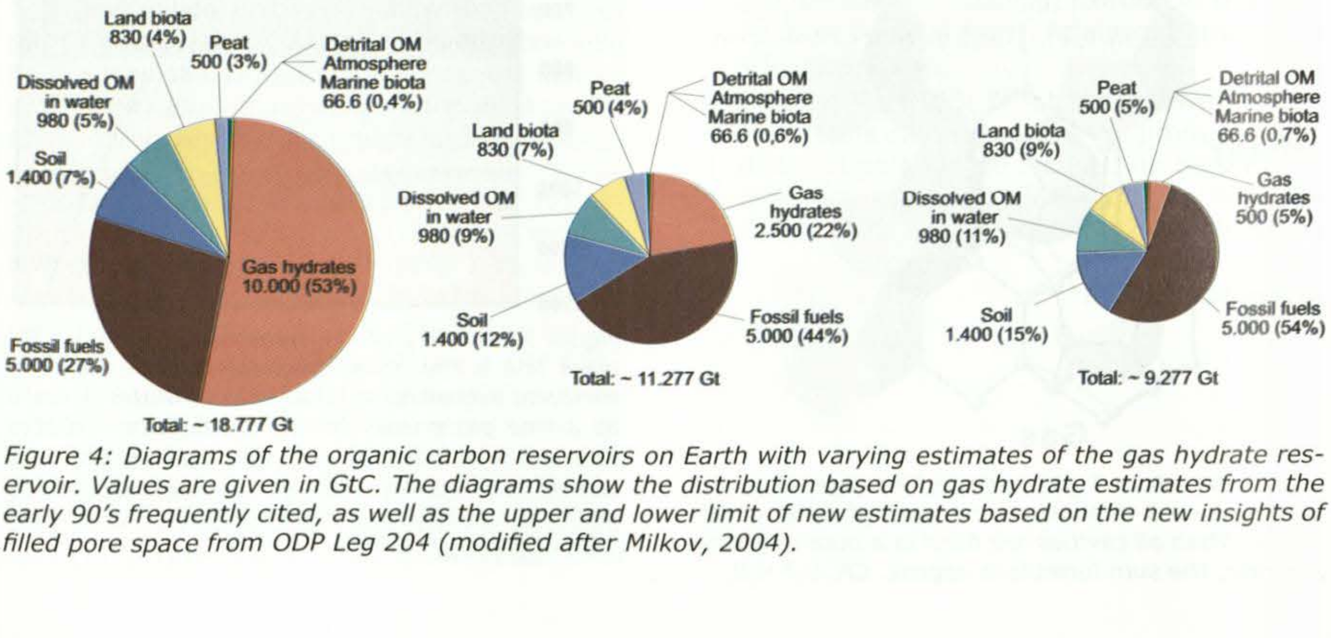

Figure 4: Diagrams of the organic carbon reservoirs on Earth with varying estimates of the gas hydrate reservoir. Values are given in GtC. The diagrams show the distribution based on gas hydrate estimates from the early 90's frequently cited, as well as the upper and lower limit of new estimates based on the new insights of filled pore space from ODP Leg 204 (modified after Milkov, 2004).

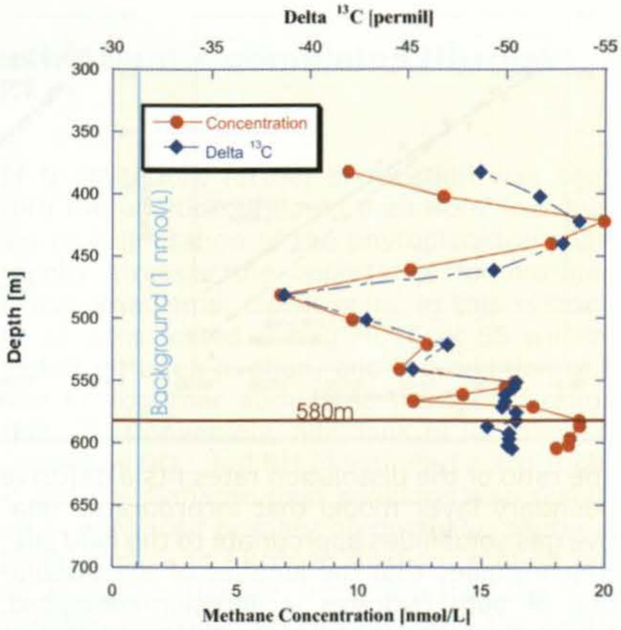

Figure 5: (a, above) Slump scars at the upper hydrate stability boundary off Costa Rica. and (b, right) methane plume above the slump scar and its stable carbon isotopic composition.

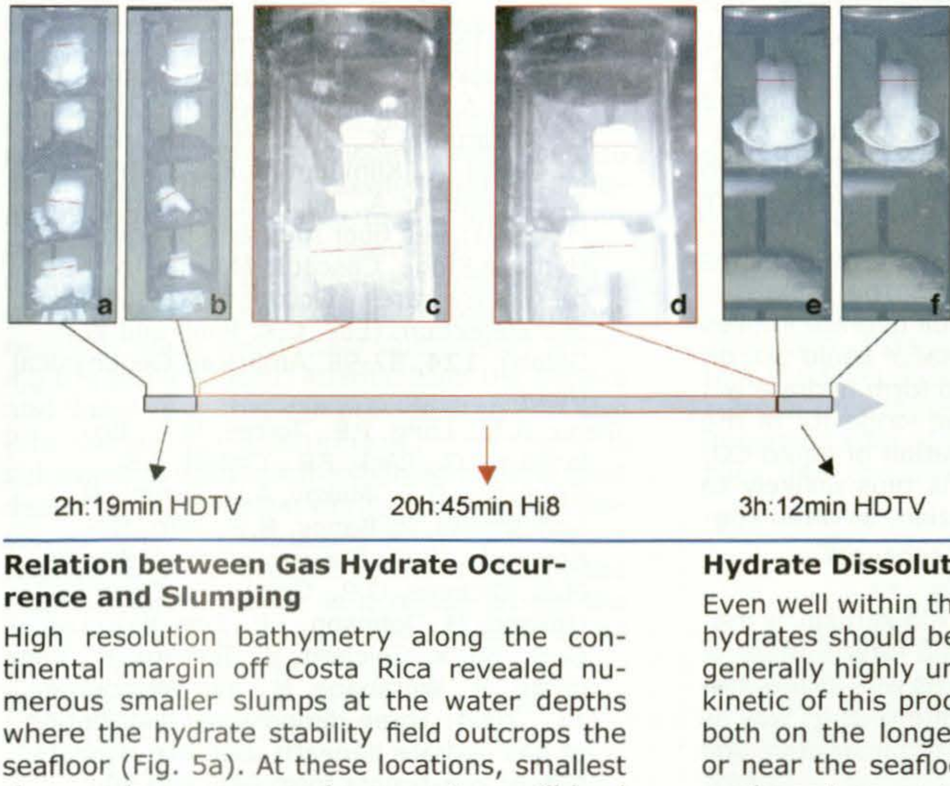

Figure 6: Overview of the evolution of the samples in the dissolution experiment. Methane hydrates are in the upper two compartments, and carbon-dioxide hydrates in the lower two. Frames are from the beginning and end of the first phase of HDTV observation (a-b), from time-lapse camera observation (c-d), and from the final HDTV observation (e-f). Only the CH_4 hydrate samples are shown in (c-f). The CO_2 hydrate samples are completely dissolved shortly after frame (c).

Relation between Gas Hydrate Occurrence and Slumping

High resolution bathymetry along the continental margin off Costa Rica revealed numerous smaller slumps at the water depths where the hydrate stability field outcrops the seafloor (Fig. 5a). At these locations, smallest changes in pressure and temperature will lead to a change from stable to unstable conditions for methane hydrates at the seafloor and vice versa. Geochemical investigation of the water column above these sites indicate active methane venting of microbial origin (Fig. 5b). The survey lead to one of the best demonstrations of enhanced abundance of slumps at the upper wedge of the hydrate stability field.

Hydrate Dissolution

Even well within the hydrate stability field, gas hydrates should be prone to dissolution in the generally highly undersaturated seawater. The kinetic of this process, which puts constraints both on the longevity of hydrate outcrops at or near the seafloor and the dynamics of the methane transport to sustain these structures, has until recently been completely unknown. In a unique deep-sea experiment, lab-grown pure methane and CO_2 hydrates were transported under pressure to the deep ocean floor (1030m) using ROV-technology and exposed to seawater with its natural CO_2 and CH_4 content and under natural current flow conditions. The dissolution caused by the contact with the undersaturated seawater was measured by monitoring the samples with HDTV-camera and a time-lapse camera system (Figs. 6,7).

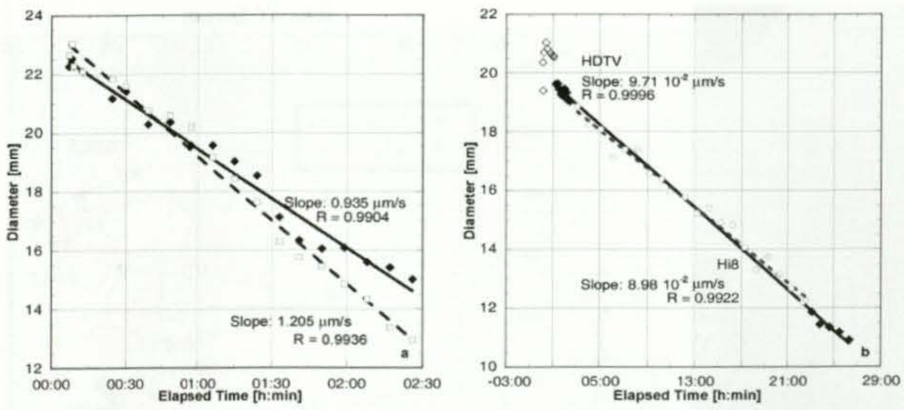

Figure 7: (a) Diameter of the CO_2 hydrate samples versus time. Upper sample: black diamonds and solid line (linear fit): Lower sample: open squares and hatched line (linear fit). (b) Diameter of the upper CH_4 hydrate sample versus time. Filled diamonds and solid line: measurements and linear fit using the HDTV observations at the beginning and the end of the experiment. Circles and hatched line: measurements and linear fit using the Hi_8 observations.

The ratio of the dissolution rates fits a diffusive boundary layer model that incorporates relative gas solubilities appropriate to the field site, which implies that the kinetics of the dissolution of both hydrates is diffusion-controlled. Dissolution of several mm methane hydrate per day in undersaturated seawater suggests that long-term survival of seafloor hydrate outcrops or hydrates close to the sediment surface observed today must be sustained by supply of sufficient CH_4 to maintain boundary layer saturation or continuous hydrate regrowth. The dissolution rate of gas hydrate might also be a key parameter controlling the supply of methane to microbial methane-oxidizing communities in hydrate bearing sediments. The rapid dissolution rate of carbon-dioxide hydrate implies that in the case of the disposal of liquid CO_2 on the sea floor, the potential to form hydrate will not significantly enhance the longevity of the released CO_2 The transformation of liquid CO_2 to hydrate on the seafloor is thus unlikely to shield bulk CO_2 from dissolution, as often suggested in CO_2 sequestration concepts.

Research on gas hydrates will remain a major focus nationally during the future phase of the Geotechnology program as well as internationally by energy-seeking interests as well as those concerned with CO_2-sequestration and climate change.

IFM-GEOMAR Contributions

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